X-RAY STUDY OF MICROSTRUCTURE AND GRAIN BOUNDARY STATISTICS IN NANOCRYSTALLINE MATERIALS

A.P. ZHILYAEV, I.V. ALEXANDROV AND R.Z. VALIEV
Institute for Physics of Advanced Materials
Ufa State Aviation Technical University
12, K. Marx St., 450000 Ufa, Russia

1. Introduction

Recently the attention of many scientists has been attracted to nanostructured materials possessing novel physical and mechanical properties [1, 2]. Nanoscale microstructures can form during processing of nanostructured materials using different methods, e.g. condensation in inert gas atmosphere, rapid quenching, electrodeposition, ball milling, severe plastic deformation and during oxidation (see [1, 3]). Among them only severe plastic deformation and ball milling give bulk nanostructured samples while others yield thin films. It is well known that internal interfaces or the grain boundaries (GB) control behavior of nanostructured materials. Such properties as strength, ductility, hardness, resistance to failure, corrosion resistance, fatigue and electromigration are all greatly affected by grain boundaries and their behavior as an whole ensemble [4-7]. Two major methods are used to characterize GB: transmission electron microscopy can analyze the atomic structure of individual grain boundaries and X-ray diffractometry may be used to examine volume-averaged characteristics. This paper presents a review of recent results obtained in ultra-fine grained (UFG), nanocrystalline (NC) metals, and oxide films using X-ray analysis. Both fine structure (crystallites' size, microdistortions) and statistical features (texture and grain boundary character distribution) have been calculated from experimental measurements. Different techniques (severe plastic deformation, electrodeposition, oxidation etc.) have been used to process metals and alloys where mean grain size is less than 1 μm for UFG and less than 100 nm for NC materials.

2. Methods of Sample Processing

Samples of Cu and Ni with UFG structure (a mean grain size less than 0.2 μm) were processed by torsion straining and equal channel angular pressing. Nanostructured nickel samples with grain size about 20 nm were made by electrodeposition. Zirconium oxide thin film formed during oxidation of Zr-2.5%Nb alloy. Mean grain size of ZrO_2 film formed is less than 50 nm by TEM.

G.M. Chow et al. (eds.), Nanostructured Films and Coatings, 215–222.

To process the UFG microstructure in bulk Cu and Ni the method of severe plastic deformation was applied. It was carried out using intense shear deformation by torsion straining under high imposed pressure of several GPa and equal channel angular pressing [3] (Figure 1).

Torsion straining under high imposed pressure of several GPa (Figure 1a) was used for fabrication of disk type samples 10 mm in diameter and 0.2 mm in thickness from massive ingot and ball milled powder as well. The logarithmic torsion strain of samples was 7 at the perimeter of the disks.

During equal channel angular pressing cylindrical ingots were machined and pressed through a special die to give a continuous repeating passage (Figure 1b). Following pressing, the samples were pressed again through the same die. Equal channel angular pressing was conducted up to 12 passes. Each pass corresponded to true strain equal approximately to 1. Equal channel angular pressing facility used in these experiments had an angle of intersection of two channels equal to 90°. The processed samples had a cross section diameter about 20 mm and the length of about 80 mm.

3. X-ray Analysis

The results of conducted experimental studies [3] indicate that a general view of X-ray diffraction patterns of nanostructured materials processed by severe plastic deformation differs from that of corresponding coarse-grained materials (Figure 2). The X-ray patterns of nanostructured materials are characterised by changed relative intensity, significant broadening, a shift in position of centroids, change in a X-ray peak profile shape and elevated diffusion background of X-rays scattering [5,9]. Note a growth of relative intensity of X-ray peak (111) in respect to other peaks that is typical for nanostructured Cu (Fig. 2) and Ni.

X-ray diffraction patterns of these materials requires their careful examination and interpretation. For example, long tails and considerable broadening lead to necessity of

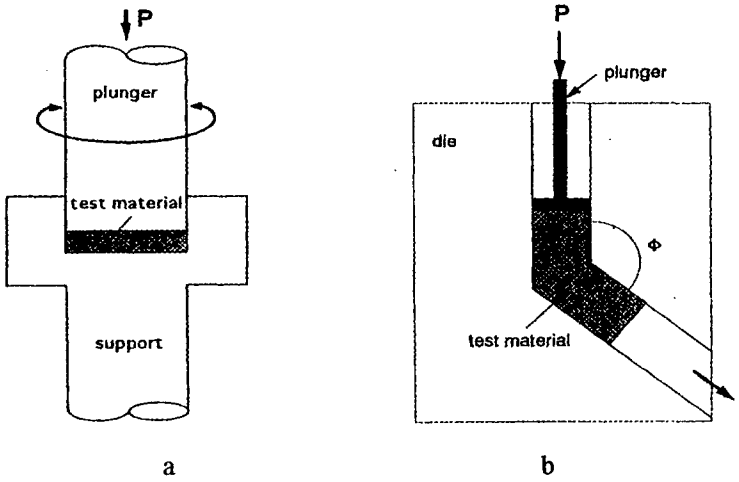

Figure 1. Principles of severe plastic deformation methods: torsion straining under high pressure (a), equal channel angular pressing (b).

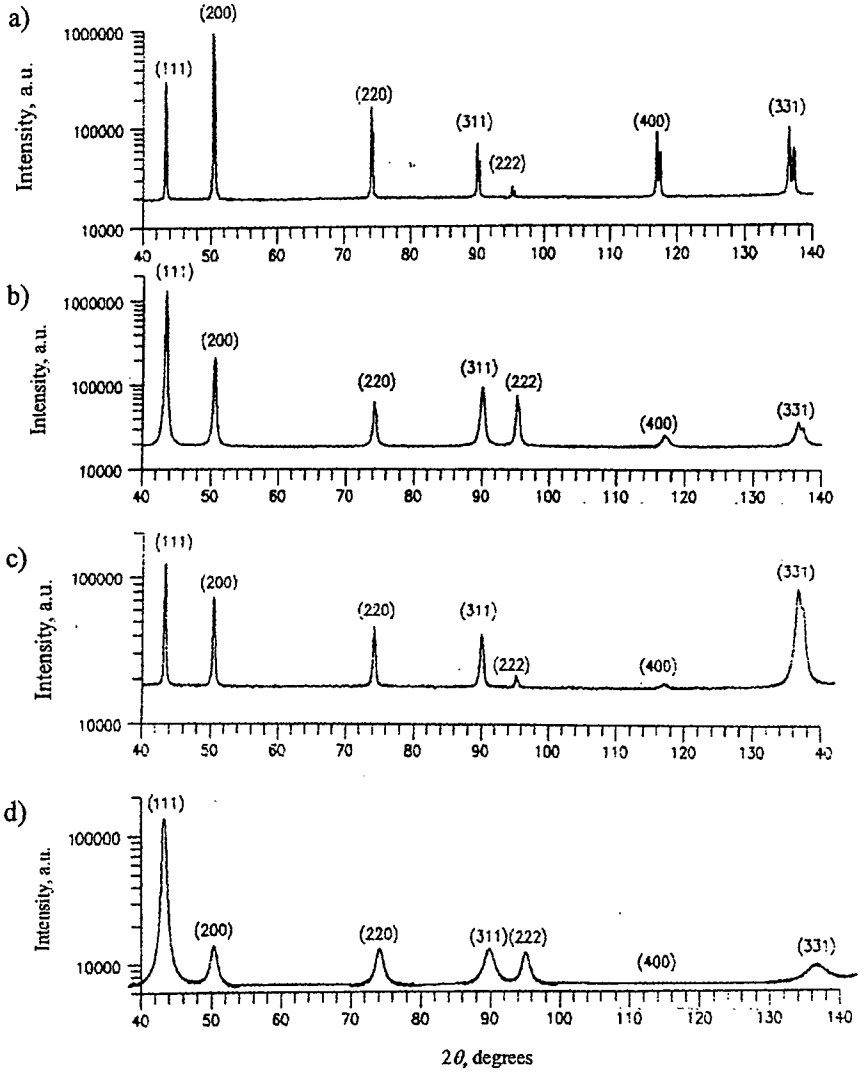

Figure 2. X-ray diffraction patterns of Cu: coarse-grained (a); nanostructured, processed by torsion straining (b), equal channel angular pressing (c), consolidation of powder by torsion straining (d).

obtaining experimental information from the very wide intervals in vicinities of X-ray peaks. The very small intensity of high angle peaks should be taken into account as well.

The changes observed in the general view of X-ray diffraction patterns testify that the evolution of structure of the studied materials resulted from severe plastic deformation. The data obtained in different experiments indicate changes in lattice parameter, structure refinement, elevated microdistortions of a crystal lattice, high static and dynamic atomic displacements, and decrease in the Debye temperature.

Moreover, severe plastic deformation results in changes in preferential orientations of grains, i.e. crystallographic texture. The low temperature experimental studies revealed that the thermal expansion coefficient α_T, equalled to $(3.75\pm0.10)\times10^{-5}$ K^{-1} in

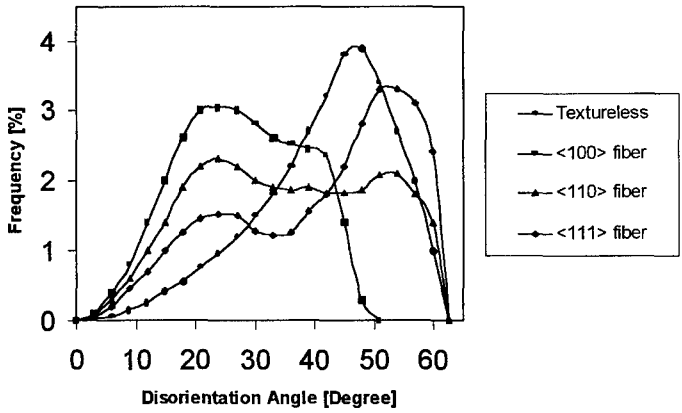

Figure 3. Disorientation angle distributions for variously textured model polycrystals

nanostructured Ni exceeds a corresponding tabular value of coarse-grained Ni by approximately a factor of 3 [9]. These observations correlate with the data of the Young's modulus measurements previously conducted by the ultrasonic method [10]. According to these data the Young's modulus in the nanostructured Cu processed by severe plastic deformation is lower than in the corresponding coarse-grained one by 12÷13%. At the same time a decrease in the Debye temperature was revealed in these nanostructured materials. Thus, in the nanostructured Ni the Debye temperature calculated on the basis of the X-ray data is equal to 293±7 K [9] which is lower than a tabular value of the coarse-grained Ni by 22%. The calculated Debye temperature in the nanostructured Cu is 233±6 K which is lower than a tabular value of the coarse-grained Cu by 23%.

4. Grain Boundary Statistics (General Consideration)

In recent years, the relationships between grain boundary misorientation distributions and texture have been studied both experimentally and by means of computer simulation [10]. While there have been attempts to derive misorientation distributions from texture data only, our studies have shown that in general the relationship between the two distributions is not straightforward but rather ambiguous. Complications arise due to the orientation correlation, which may exist between various crystallites of the polycrystalline aggregate. These two factors, texture and orientation correlations, determine the grain boundary character distribution in a sample. Contributions of these factors to the misorientation distribution as a whole and to the fractions of specific grain boundary types are dependent on the material. In some materials, for example b.c.c. alloys, grain boundary distribution is primarily determined by texture [11]. However, the orientation correlations play a dominant role in f.c.c. alloys. The same may be true for other materials with a high propensity to formation of special (twin) boundaries. The results obtained on nanocrystalline monoclinic zirconia film give evidence in favor of this conclusion. That the misorientation distribution depends on texture can be seen e.g. from Fig. 3, which displays the misorientation angle distributions for differently textured model polycrystal with the cubic crystal lattice. Of course, the use of texture

data for evaluating the grain boundary misorientation (and hence character) distribution is very attractive because the determination of grain boundary statistics is much more laborious and time-consuming as compared to the texture measurement. However, such an approach must be treated with caution since the spatial correlations between neighboring grain orientations may have a dominant effect in the grain boundary statistics. The procedure of evaluation of the misorientation distribution from the texture data consists of assigning orientations corresponding to some model or real orientation distribution function (ODF) to a model set of grains and computing misorientations at the boundaries between these grains. Detailed description of the technique can be found elsewhere [4-7].

4.1. EXAMPLES OF DIFFERENT MATERIALS

4.1.1. BCC Materials

The data accumulated to date indicate that the role (contribution) of texture and orientation correlations in the misorientation distribution depends on the type of material. Apparently, there are little orientation correlations in metals and alloys with the BCC crystal structure. Therefore, obtaining the grain boundary character distribution directly from the experimentally determined ODF, as was done e.g. for a Fe-6%Si alloy [12], seems to produce reasonable results for such materials. Some selected results from paper [13] are presented in Table 1.

TABLE 1. Percentages of some grain boundary types in an electrical steel

GB Type	Σ3	Σ5	Σ7	Σ9
Simulation	2.2	0.9	1.0	1.0
Experiment	2.8	0.8	0.8	1.0

4.1.2. FCC Materials

On the other hand, experimental data show that the grain boundary distributions in FCC materials are dominated by the correlations in the orientations of contiguous grains. In aluminum the predominant type of correlation is the formation of low-angle boundaries, with the formation of twin (Σ3) boundaries being the secondary correlation. The grain boundary character distribution obtained from the experimentally (x-ray) determined ODF assuming these correlations, agrees well with the grain boundary distribution measured independently using transmission electron microscopy [9] (see Table 2). We must admit, however, that the agreement between the simulated and experimental misorientation angle and axis distributions was not as good as in the case of the Σ-distributions.

TABLE 2. Percentages of different grain boundary types in some fcc materials

GB Type	Aluminum		AISI 316L	
	Experiment	Simulation	Experiment	Simulation
LAB, θ<15°	30.0	32.4	8.9	7.3
Σ3	4.0	2.6	33.1	27.6
Random	66.0	65.0	58.0	65.1

4.1.3. *Zirconium Oxide Films*

TABLE 3. Percentages of different grain boundary types in ZrO_2 formed on Zr-2.5%Nb alloy during oxidation.

GB Type	Grain Growth Texture	Fiber Texture [001]	Mixture
LAB, θ<15°	–	11,4	2,1
Σ3	33,4	12,1	–
Σ71	66,6	13,6	–
Random	–	62,9	97,9

Recently, an interesting type of twin boundaries has been observed in corrosion films formed on a zirconium alloy [14]. The oxide layer consists of predominantly monoclinic zirconia with crystallite dimensions in the nanometer range. Vast areas in the film contain zirconia grains of only eight distinct orientations. These orientations can be explained by growth of zirconia crystallites in the [001] and [100] directions of the monoclinic lattice with misorientations between adjacent grains described by the 180° and 90° rotations about the above axes. In such areas only few types of intercrystallite boundaries are possible, all of them being special, coherent and semi-coherent twins and pseudo-twins. Unlike the cubic structure, where there is only one type of twin boundary – Σ3, several non-equivalent twin variants are possible in the monoclinic lattice, and grain boundary networks built entirely of twins are possible in zirconia. In this particular case, exchange of grain positions would create the grain boundaries of the same set, i.e. the grain boundary character distribution would not change. Thus, a specific strong crystallographic texture in such regions of the microstructure is determined by the correlations that provide for certain special misorientations between contiguous crystallites.

4.1.4. *Nickel Oxide Films Formed At Single Crystal Of Nickel*

TABLE 4. Percentages of different grain boundary types in NiO formed on (100) and (111) crystal faces of Ni

GB Type	(100) Substrate	(111) Substrate
LAB, θ<15°	40.4	6.4
Σ3	3.1	27.6
Random	56.5	66

Grain boundary diffusion of reactants in oxide layers makes a dominant contribution to the transport mechanisms during the oxidation of metals at temperatures less than one half of the melting point of the oxide. Qualitative evidence for the importance of grain boundary transport was found in recent work [15, 16] where it was shown that the difference between the oxide growth rates on (100) Ni and (111) Ni crystals is more than one order of magnitude. The microstructural examination indicates that this difference cannot be attributed solely to the density of short circuits paths but the character of individual grain boundaries should also be considered. A computer model

was developed to simulate the diffusion of Ni through both the grain boundaries and lattice in NiO at elevated temperatures. The grain boundary network was defined by the shape and size of oxide grains and by the grain boundary character distribution. Two sets of GBCD describing the oxide grown on (100) and (111) crystals faces of Ni (Table 4) were employed to simulate transport through the NiO film. The model was found to be effective in predicting of the difference in diffusivity through the nickel oxide grown on (100) and (111) faces. The ratio of parabolic constants for NiO for two different oxide films obtained from simulation equals 11 while from the experiments this ratio found is 14. It proves that the GBCD greatly influence and control the Ni diffusion through NiO layer.

5. Concluding Remarks

The conducted experimental X-ray structural studies showed that X-ray diffraction patterns of nanocrystals processed by severe plastic deformation significantly differ from the corresponding coarse-grained ones. These differences consist in significant broadening, shift of positions of centroids, change in X-ray peak profile shape and increase in diffusion background of X-rays scattering.

The significance of grain boundary character distribution discussed in this paper is that GBCD can vary in metals with different type of crystalline lattice, texture and microstructure. These affect spatial correlation in orientation of neighbours determining grain boundary clustering.

Acknowledgments. One of the authors, A.P.Zhilyaev would like to thank Drs. V.Yu.Gertsman and F. Czerwinski for helpful discussion of the results.

6. References

1. Schiøltz J.,D., Di Tolla Francesco and Jacobsen K. W. (1998) Softening of nanocrystalline metals at very small grain sizes, *Nature* **391**, 561–563.
2. McFadden S. X., Mishra R S., Valiev R. Z., Zhilyaev A. P. and Mukherjee A. K. (1999) Low-temperature superplasticity in nanostructured nickel and metal alloys, *Nature* **398**, 684-686.
3. Valiev R. Z., Islamgaliev R. K. and Alexandrov I. V. (1999) Bulk nanostructured materials processed by severe plastic deformation, *Progress in Material Science* (accepted for publication).
4. Gertsman V. Y., Zhilyaev A. P., Pshenichnyuk A. I., and Valiev R. Z. (1992) Modeling of grain boundary spectrum in polycrystals with crystalllographic texture, *Acta Metall. Mater.* **40**, 1433-1441.
5. Zhilyaev A. P., Gertsman V. Y., Mishin O. V., Pshenichnyuk A. I., Aleksandrov I. V. and Valiev R. Z. (1993) Grain boundary misorientation spectra determined by real ODF in f.c.c. materials susceptible to annealing twinning, *Acta Metall. Mater.* **41**, 2657-2665.

6. Gertsman V. Y., Tangri K.and Valiev R. Z. (1994) Overview No.116: On the grain boundary statistics in metals and alloys susceptible to annealing twinning, *Acta Metall. Mater.* **42,** 1725-1804.
7. Zhilyaev A. P., Pshenichnyuk A. I., and Valiev R. Z. (1994) Energetical approach to modelling grain boundary misorientation spectrum determined by real ODF, *Strength of Materials (Proc. Int. Conf.),* Eds. H.Oikawa et al, Sendaii: JIM, 997-890.
8. Alexandrov I. V., Zhang, K., Kilmametov A. R., Lu, K., Valiev R. Z. (1997) The x-ray characterization of the ultrifine-grained Cu processed by different methods of severe plastic deformation, *Materials Science & Engineering* **A234-236**, 331-334.
9. Zhang K., Alexandrov I.V., Kilmametov A. R., Valiev R.Z., Lu K., (1997) The crystallite-size dependence of structural parameters in pure ultrafine-grained copper. *J. Phys. D: Appl. Phys.* **30**, 3008-3015.
10. Mulyukov R. R., Akhmadeev N. A., Valiev R. Z., Mikhailov S. B. (1993) Strain amplitude dependence of internal friction and strength of submicrometre-grained copper, *Materials Science and Engineering* **A131**, 143-149.
11. V.Y.Gertsman, A.P.Zhilyaev and J.A.Szpunar (1998) On the role of orientation correlations in the grain boundary character distribution in textured polycrystals, in *Proceedings of ICGG-III.* (accepted for publication).
12. Morawiec A., Szpunar J. A. and Hinz D. C. (1993) Texture influence on the frequency of occurrence of CSL-boundaries in polycrystalline materials, *Acta Metall. Mater.* **41**, 2825-2832.
13. Hayakawa Y., Szpunar J. A., Palumbo G. and Lin P. (1996) The role of grain boundary character distribution in Goss texture development in electrical steels. *J. of Magnetism and Magnetic Materilas* **160** 143-144.
14. Gertsman V. Y., Lin Y. P., Zhilyaev A. P. and Szpunar J. A., Special grain boundaries in zirconia corrosion films. *Phil. Mag.* (accepted for publication)